

WHAT IS CLAIMED IS:

1. A method for determining the presence and concentration
5 of gases by means of monitoring the change in photons in a sensing
system comprising passing photons though a waveguide, which is
coated with a porous transparent material and impregnated with a
sensing media: and further comprising a mean to couple the optical
signal in the waveguide to the sensing material in the coating via
10 evanescent wave absorption, and further comprising a display means,
and further comprising at least one sensor which response to at
least one target gas and can be monitored by an electronic circuit
and further comprising a photon emitter and a photon detector.

15 2. A method as claimed in claim 1 further comprising at
least one optically responding sensor(s), which is monitored by a
photon source and photodetector and is calibrated to initiate a
signal at a predetermined level of target gas for a predetermined
period of time, the method comprising the steps of:

20 intermittently measuring the optical (transmission)
characteristics of the sensor(s); and calculating the amount of
target gas present.

25 3. A claim as in claimed 1 further comprising a means of
differential measurement from a control sensor not exposed to the
target gas, and further comprising a control sensor that responds to
the environment the same as the target gas sensor with the same
optical characteristic changes over time temperature, humidity,
smog, and other conditions as the gas sensor; and further a means to
30 prevent the target gas from reacting to the control sensor.

4. A claim as in claim 1 where the target gas is carbon
monoxide.

5. An apparatus that measure the identity and concentration
of gases and vapors comprising at least one optical evanescent field
5 absorption sensor; and further comprising a photon emitter and
photon detector; and further comprising a waveguide coated with a
porous transparent material.

10 6. An apparatus as claimed in claim 5 comprising a porous
transparent material that is an oxide; and further comprising a
sensing material coated onto the transparent porous oxide that
changes its optical properties when exposed to a target gas.

15 7. An apparatus as claimed in claim 5 comprising a set of
EFA sensors that respond to a variety of target gases and the
identity of the target gas is determined by the wavelengths and
intensity of the absorption.

20 8. An apparatus as claimed in claim 6 comprising a ring
waveguide coated with a sensing material; and further comprising a
straight waveguide section and a means to couple photons from the
straight waveguide to the ring waveguide and remove a portion of
those photons and then detect a target gas by monitoring the amount
of photons at the end of the straight waveguide.

25 9. An apparatus as claimed in claim 6 where the target gas
is carbon monoxide.

30 10. An apparatus as in claim 9 wherein the sensing material
is a chemical reagent comprising at least one of the
following groups:

Group 1 Palladium salts selected from the group consisting of
palladium sulfate,
chloride, bromide.

5 Group 2 Heteropoly(molybdates such as silicomolybdic acid,
ammonium

5 molybdate, alkali metal molybdates

Group 3 Copper salts of sulfate, chloride, bromide and
perchlorate.

10 Group 4 Alpha. beta gamma or delta cyclodextrins and there
hydroxymethyl ethyl and propyl derivatives.

10 Group 5 Soluble salts of alkaline and alkali chlorides and
bromides and mixture thereof;

15 Group 6 Organic solvent and/or co-solvent and trifluorinated
organic anion selected from the group including dimethyl sulfoxide
(DMSO), tetrahydrofuran (THF), dimethyl formamide (DMF),
trichloroacetic acid, trifluoroacetate, a soluble metal
trifluoroacetylacetone selected from cation consisting of copper,
calcium, magnesium, sodium, potassium, lithium, or mixture thereof;
and

20 Group 7 Soluble inorganic acids such as hydrochloric acid,
sulfuric acid, sulfurous acid, nitric acid, and strong oxidizers
such as peroxide, or mixture thereof.

25 11. A method as claimed in claim 1 comprising the process of
fabricating the EFA sensing device comprising the steps of coating
the waveguide with a porous silica layer between 20 nm and 200 nm
and then coating the porous silica surface with a sensing agent.

30 12. The method as claimed in claim 11 wherein the step of
coating the waveguide is to immerse the waveguide in a chemical
reagent comprising at least one of the following groups for several
hours:

Group 1 Palladium salts selected from the group consisting of
palladium sulfate, chloride, bromide and mixture thereof;

35 Group 2 Heteropoly(molybdates such as silicomolybdic acid,
ammonium molybdate, alkali metal molybdates

Group 3 Copper salts of sulfate, chloride, bromide and mixtures thereof,

5 Group 4 Alpha, beta, gamma, and or delta cyclodextrins and their derivatives and mixtures thereof,

Group 5 Soluble salts of alkaline and alkali chlorides and bromides and mixture thereof;

10 Group 6 Inorganic or organic acid and or salt of organic or inorganic compound that dissolve in the mixture in the presence of the acid(s); and

15 Group 7 Strong oxidizer such as nitric acid, hydrogen peroxide or mixture thereof and further removing the waveguide and porous outer layer from the solution and then dry the waveguide system slowly over 1 to 2 days to form the supramolecular sensing complex.

13. A method of producing the porous transparent layer which provide the sensing platform for a sensing agent in evanescent filed absorption sensor is made by starting with a silicon alkoxide; and further comprising the step of reaction the silicon alkoxide with a organic material with carbons from 4 to 12; and further in voles hydrolysis of the complex to for an Organo-silicon compound that is stable a soluble in non-polar solvents and further dissolving the solid Organo-silicon in the solvent and then coating the waveguide 20 with the solution and further drying the coating and then heating it 25 to drive off the ^{vap} solvent.

14. The method of claim 13 further comprising the steps of adding a pore forming agent to the solvent containing the organo-silicon; and then coating the waveguide, drying and heating to remove all solvent and to burn out the pore forming agent that results in a 150 to 300 nm pore structure.

15. The method of claim 14 wherein the pore agent is a 35 soluble polymer of more than 100 carbons.

16. A method of measuring the concentration of carbon monoxide using a porous transparent monolith that is coated with a
5 chemical sensing agent comprising an optical cavity that surrounds the sensor on at least 2 reflective surface facing each other with the sensor in between them and there is further a photon source that emits photons that are pass through the sensor monolith and are then
10 striker the reflector; and further the photons are reflected of the surface and direct to pass through the sensor again and this process repeat at least one more cycle striking the second reflector and being direct to pass through the transparent sensor place between
15 the reflectors that response with an optical change proportional to the CO exposure ands the speed of detection proportional to the number of times the photon beam passes though the sensor before striking the photon detector.

17. A method as claimed in claim 16 that comprises a silica porous monolith with average pore diameter of 10 to 30 nm and the
20 sensing agent is applied by immerse the porous transparent silica monolith in a chemical reagent comprising at least one of the following groups for several hours:

25 Group 1 Palladium salts selected from the group consisting of palladium sulfate, chloride, bromide and mixture thereof;

Group 2 Heteropolymolybdates such as silicomolybdic acid, ammonium molybdate, alkali metal molybdates

Group 3 Copper salts of sulfate, chloride, bromide and mixtures thereof,

30 Group 4 Alpha, beta, gamma, and or delta cyclodextrins and their derivatives and mixtures thereof,

Group 5 Soluble salts of alkaline and alkali chlorides and bromides and mixture thereof;

35 Group 6 Inorganic or organic acid and or salt of organic or inorganic compound that dissolve in the mixture in the presence of the acid(s); and

5 Group 7 strong oxidizer such as hydrogen peroxide and or
nitric acid. and further removing the waveguide and porous outer
layer from the solution and then dry the waveguide system slowly
over 1 to 2 days to form the supramolecular sensing complex.

10 18. A method as claimed in claim 17 where the porous silica
is made by a solgei method and the average pore diameter id 16 nm to
27 nm.

15 19. A method as claimed in claim 14 comprising a process for
monitoring the response of a set of EFA sensors; and further
comprising a means to determine the value of one or more target gas
concentrations in a fashion so as to rapidly determine the danger
levels, TWA, total dose, and peak concentration over a pre-selected
period.

20 20. An apparatus as claimed in claim 10 where the device
comprises a microprocessor and where there is are several photon
sources of different
wavelengths and at least one photon detector and there is a means to
measure each wavelength separately by pulsing the photon source at
different time and reading the many different wavelengths; and
25 further an analog to digital converter to convert the analog signal
to digital and further comprise a means to store the digitized
signal from each wavelength and compare the signal patterns form
each wavelength to a pattern stored in the microprocessor and an
algorithm that will interpret the various signal patterns to
30 identify the gases present and estimate their concentrations.

35 21. An apparatus as claimed in claim 5 comprising a waveguide
in the shape of a ring and further comprising a very thin coating on
the ring with a sensing material in the coating; and further
comprising a straight waveguide in the immediate vicinity and

1 45915/GTL/Q8

running tangent to the ring waveguide and a means to switch the
photons from the straight waveguide to the ring waveguide and a
5 means to switch the photon from the ring back to the straight
waveguide and a means to detect the change in evanescent field
absorption due to one or more target gases by monitoring the amount
of photons at the end of the straight waveguide.

10 22. An apparatus as claimed in claim 21 comprising more than one
light source each with different wavelengths and a means to read each
wavelength independently.

15 23. An apparatus as claimed in claim 22 further comprising
several photon sources of different wavelengths and at least one photon
detector and there is a means to measure each wavelength separately by
pulsing the photon source at different time and reading the many
different wavelengths; and further an analog to digital converter to
convert the analog signal to digital and further comprise a means to
20 store the digitized signal from each wavelength and compare the signal
patterns form each wavelength to a pattern stored in the microprocessor
and an algorithm that will interpret the various signal patterns to
identify the gases present and estimate their concentrations.

25 24. A multi-pass photon sensing gas detector apparatus for
determining the target gas concentration and identity comprises: a
microprocessor and a means for assigning sensor reading values to each
of the measured optical characteristics; means for determining
differences between sensor reading values;

30 memory for storing the differences; an alarm register for adding
the sum of a plurality of the differences stored in the memory; and
means for entering an alarm mode when value of the alarm register
exceeds an alarm point; and further comprising a sensing system as
follows: a porous transparent monolith "that is coated with a chemical
35 sensing agent comprising an optical cavity that surrounds the sensor

on at least 2 reflective surface facing each other with the sensor in
between them and there is further a photon source that emits photons
5 that are pass through the sensor monolith and are then strike the
reflector; and further the photons are reflected off the surface and
direct to pass through the sensor again and this process repeat at
least one more cycle striking the second reflector and being direct to
10 pass through the transparent sensor place between the reflectors that
response with an optical change proportional to the CO exposure and
the speed of detection proportional to the number of times the photon
beam passes though the sensor before striking the photon detector.

15 25. A multi-pass photon gas detection apparatus as claimed in
24 comprising a means to optically sense at least two sensors in a
differential measuring system comprising:

20 an optical means to sense the target gas; a control optical means
for sensing the environment the same as the target gas sensor but does
not respond to the gas;

25 measuring means for measuring the difference in the
characteristics of the sensor; and control;

means for determining magnitude of the measured difference in
optical characteristics and the intensity of the difference, including
a means to monitor accurately the target gas concentration when first
25 sensor responding to the target gas and control sensor regenerates so
fast no optical response is seen.

26. A multi-pass photon gas detection apparatus as claimed in
claim 25 comprises:

30 at least one photon source; and at least one photodetector
optically coupled with the sensor and the photon source for producing
a photocurrent proportional to the measured characteristics of the
sensor; and

35 further comprising a control sensor and a means to measure the
difference between any CO sensor and the control a capacitor coupled

1 45915/GTL/Q8

to the photodetector, the capacitor being charged by the photocurrent; and

5 a microprocessor coupled to the capacitor for measuring time for charge on the capacitor to reach a threshold, the measured time being proportional to the darkness of the sensor.

10 27. A multi- pass photon gas detection apparatus as claimed in
claimed 25 comprising an A to D converter to digitize the signal from
the photodetector; and

further comprising a means to incorporate the device into a fuel cell vehicle to control the reformer process by measuring CO in milliseconds; and

15 further comprises a sensor to selectively detect CO in the presence of hydrogen and CO₂; and further comprising a porous transparent monolith that is coated with a chemical sensing agent comprising an optical cavity that surrounds the sensor on at least 2 reflective surface facing each other with the sensor in between them and

20 there is further a photon source that emits photons that are pass through the sensor monolith and are then strike the reflector; and further the photons are reflected off the surface and direct to pass through the sensor again and this process repeat at least one more cycle striking the second reflector and being direct to pass through the transparent sensor placed between the reflectors that response with an optical change proportional to the CO exposure and the speed of detection proportional to the number of times the photon beam passes though the sensor before striking the photon detector.

25 30 28. An evanescent photon absorption sensor based gas detector apparatus as in claim 6 comprising at least 2 sensors and sensor monitoring system and a means to condition the sample and a means to switch the gas from the reformatte stream to a air stream and back periodically; and further comprising a microprocessor control the

1 45915/GTL/Q8

switching and to process and digitize the signals from the photodetector(s) to determine the CO gas concentration in a fuel cell reformate stream, and further comprising a means to incorporate the device into a fuel cell vehicle to control the reformer process by measuring CO in milliseconds; and further comprises a sensor to selectively detect CO in hydrogen and CO₂, a means indicate need of service, and a means to protect the occupants from the gases detected.

10

29. An evanescent photon absorption sensor based gas detector apparatus as claimed in claim 28 further comprising:

at least two photon sources in each sensing chamber;
at least one photodetector optically coupled to receive photons from the photon sources as modified by the sensor and at least two photon source for emitting photons at different wavelengths that in term measure the response of the sensor(s) to CO and humidity; and a means to determine the CO and humidity component to the signal; and
further comprising a chemical reagent comprising at least one of the following groups for several hours:

Group 1 Palladium salts selected from the group consisting of palladium sulfate, chloride, bromide and mixture thereof;

Group 2 Heteropolytungstate such as silicomolybdic acid, ammonium molybdate, alkali metal molybdates

Group 3 Copper salts of sulfate, chloride, bromide and mixtures thereof,

Group 4 Alpha, beta, gamma, and or delta cyclodextrins and their derivatives and mixtures thereof,

Group 5 Soluble salts of alkaline and alkali chlorides and bromides and mixture thereof;

Group 6 Inorganic or organic acid and or salt of organic or inorganic compound that dissolve in the mixture in the presence of the acid(s).

35

30. An evanescent photon absorption sensor based gas detector apparatus as claimed in claim 2 comprising a means for controlling the
5 reformer of a fuel cell where the device comprises a microprocessor and where there is are several photon sources of different wavelengths and at least one photon detector and there is a means to measure each wavelength separately by pulsing the photon source at different time and reading the many different wavelengths; and further an analog to
10 digital converter to convert the analog signal to digital and further comprise a means to store the digitized signal from each wavelength and compare the signal patterns form each wavelength to a pattern stored in the microprocessor and an algorithm that will interpret the various signal patterns to identify the gases present and estimate their
15 concentrations.

31. An evanescent photon absorption sensor based gas detector apparatus as claimed in claim 6 comprising two sensors in two separate housing each comprising more than one photon source each of a different wavelength; and further comprising a sample conditioning system that consist of a thermoelectric cooling section and a heating section, between the cold section and the heating section is a membrane to prevent water from passing and a means to periodically remove excess water; and further comprising

25 the CO detector system with at least two separate chambers with valves connecting the sensors alternately to the air and a reformatte gas sample; further comprising a display means to indicate the need to perform maintenance; and further comprising at least two sensor, which one responses to the CO in the hydrogen stream while at least one remains outside the stream and is regenerated in clean air, and further comprising a means to switch the flows of clear air through one of the sensor chambers and a portion of the hydrogen stream through another sensor chamber and a control means to assure that the concentration of CO directed to the fuel cell is less than a pre- determined; and
30 further comprising and further comprising at least two optically
35

5 responding sensors, which response to the CO and humidity; and can be
monitored by a low-powered electronic circuit with a current draw of
less than 25 microamps; and further comprises a supramolecular complex
that is self assembled on to a semi-transparent silica porous
substrate; and further comprising a thin semi-transparent sensing layer
on the porous transparent substrate comprising palladium, copper and
calcium metals ions, halogen anions and cyclodextrins and there
10 derivatives and an acid.

25 32. A method as in claim 13 comprising a process at least one
optically responding sensor(s) monitored by two different photon
sources and a photodetector and the system is calibrated to initiate
15 a signal at a predetermined level of target gas for a predetermined
period of time, the method comprising the steps of: intermittently
measuring the optical (transmission) characteristics of the sensor(s);
and further comprising a means to monitor a reformat stream by
sampling the stream alternately as a means to alternately direct a
20 sample of gas to the first sensor and air to the second sensor and the
to reverse the process to allow the first sensor to regenerate and
further comprising a sample condition means so that sample of reformat
and air enter the sensing chambers at a predetermined relative
humidity, pressure and temperature.

25 33. A device as claimed in claim 5 further comprising micron
size sensors that can modify their photon properties to signal an
indication of a gas detection, which is proportional to changes in the
way photon interact with the material.

30 34. An apparatus a claimed in claim 28 further comprising a that
is use to calculate the CO concentration and further a means to display
the digital value of the CO concentration, further comprising a mean
to measure an compensate for temperature value; and further comprising
35 a sensor which consist of a porous silica materials coated with a

chemical reagent comprising at least one of the following groups: Group
1: Palladium salts selected from the group consisting of palladium
5 salts of sulfate, palladium sulfite, palladium pyrosulfite, palladium
chloride, palladium bromide, palladium iodide, palladium perchlorate,
CaPdCl₄, CaPdBr₄, Na₂PdCl₄, Na₂PdBr₄, K₂PdCl₄, K₂PdBr₄, Na₂PdBr₄,
CaPdCl_xBr_y, K₂PdBr_xCl_y, Na₂PdBr_xCl_y (where x can be 1 to 3 if y is 4 or
visa versa), and organometallic palladium compounds such as palladium
10 acetamide tetrafluoroborate and other similarly weakly bound ligands,
and mixtures of any portion or all of the above; Group 2: Molybdenum,
vanadium, and/or tungsten salts or acid salts selected from the group
consisting of silicomolybdic acid, phosphomolybdic acids, and their
soluble salts, molybdenum trioxide, ammonium molybdate, alkali metal,
15 or alkaline earth metal salts of the molybdate anions, mixed
heteropolymolybdates, or heteropolytungstenates and mixtures of any
portion or all of the above; Group 3: Soluble salts of copper halides,
sulfates, nitrates, perchlorate, and mixtures thereof, copper
organometallic compounds that regenerate the palladium such as copper
20 tetrafluoroacetic acid, copper tritluoroacetylacetone, and other
similar copper compound, and copper vanadium compounds such as copper
vanadate, and soluble vanadium compounds that can be incorporated into
the group 2 molybdenum based-keg ions such as phosphomolybdic acid and
silicomolybdic acid, and mixtures of any portion or all of the above;
25 Group 4: Supramolecular complexing molecules selected from the
cyclodextrin family including alpha, beta, and gamma as well as their
soluble derivatives such as hydroxymethyl, hydroxyethyl, and
hydroxypropyl beta cyclodextrin, crown ethers and their derivative, and
mixtures of any portion or all of the above; Group 5: Soluble salts of
30 alkaline and alkali halides, and certain transitional metal halides
such as manganese, cadmium, cobalt, chromium, nickel, zinc, and other
soluble halide such as aluminum; and any mixture thereof; Group 6:
Organic solvent and/or co-solvent and trifluorinated organic anion
selected from the group including dimethyl sulfoxide (DMSO),
35 tetrahydrofuran (THF), dimethyl formamide (DMF), trichloroacetic acid,

1 45915/GTL/Q8

trifluoroacetate, a soluble metal trifluoroacetylacetone selected from
cation consisting of copper, calcium, magnesium, sodium, potassium,
5 lithium, or mixture thereof; Group 7: Soluble inorganic acids such as
hydrochloric acid, sulfuric acid, sulfurous acid, nitric acid, and
strong oxidizers such as peroxide, or mixture thereof.

35. The apparatus of claim 28 wherein the microprocessor
10 comprises a means for assigning sensor reading values to each of the
measured photon characteristics; means for determining differences
between sensor reading values;

memory for storing the differences;

15 an alarm register for adding the sum of a plurality of the
differences stored in the memory; and

means for entering an alarm mode when value of the alarm register
exceeds an alarm point and a means to signal when the change has
occurred above a predetermined level.

20 36. An apparatus as claimed in 29 comprising a means to sense
at least two sensors in a differential measuring system comprising:

a photon sources and detector means to sense the target gas ; a
control means for sensing environment parameters that affect the target
gases and compensate for those changes;

25 a means for measuring the difference in the characteristics of
the sensor; and a means for determining magnitude of the measured
difference in photon characteristics and the intensity of the
difference, including a means to monitor accurately the target gas
concentration under a wide range of temperature and humidity.

30 37. A gas sensing gas detector apparatus for determining the
target gas concentration comprises: a photon source and a sensor that
changes its index of refraction when exposed to the target gas; and
further comprising

35

two waveguides one located on opposite sides of the sensor; and
further comprising a means to measure the intensity of photon that are
5 switched from waveguide 1 which is illuminated by the photon source to
second waveguide proportional to the concentration of target gas; and
further comprising a means for entering an signal or control mode when
value of photon intensity changes exceeds a predetermined level; and
10 further comprising a sensing system comprising a porous transparent
monolith that is coated with a chemical sensing agent comprising an
optical element coupling the two waveguides and further

the sensor in between the two waveguides pass photons from first
waveguide to the second waveguide in proportion to the amount of target
gas exposed to the sensor.

15 38. A gas detection apparatus as claimed in 37 comprising a
means to optically sense at least two sensors in a differential
measuring system comprising:

20 an optical means to sense the target gas ; a control optical
means for sensing the environment the same as the target gas sensor but
does not respond to the gas;

measuring means for measuring the difference in the
characteristics of the sensor; and control

25 means for determining magnitude of the measured difference in
optical characteristics and the intensity of the difference, including
a means to monitor accurately the target gas concentration when first
sensor responding to the target gas and control sensor regenerates so
fast no optical response is seen.

30 39. A gas detection apparatus as claimed in claim 37 comprises:
at least one photon source; and at least one photodetector optically
coupled with the sensor and the photon source for producing a
photocurrent proportional to the measured characteristics of the
sensor; and further comprising a control sensor and a means to measure
35 the difference between any CO sensor and the control

a capacitor coupled to the photodetector, the capacitor being charged by the photocurrent; and

5 a microprocessor coupled to the capacitor for measuring time for charge on the capacitor to reach a threshold, the measured time being proportional to the darkness of the sensor.

10 40. A miniaturized porous substrate less than one micron in any dimension coated with a sensing chemical that response by changes its optical transmission to carbon monoxide comprising a photon source and a photon detector; and

further comprising a microprocessor to control the photon sources and the photon detector.

15 41. A very small sensing device as claim in claimed in 40 comprising a porous transparent substrate and further comprising a chemical reagent coated onto the high surface area of the porous substrate and further comprising at least one of the following groups 20 of compounds to form a CO sensing material:

Group I Palladium salts selected from the group consisting of palladium sulfate, chloride, bromide and mixture thereof;

Group 2 Heteropolytungstate such as silieomolybdic acid, ammonium molybdate, alkali metal molybdates

25 Group 3 Copper salts of sulfate, chloride, bromide and mixtures thereof,

Group 4 Alpha, beta, gamma, and or delta cyclodextrins and their derivatives and mixtures thereof,

30 Group 5 Soluble salts of alkaline and alkali chlorides and bromides and mixture thereof;

Group 6 Inorganic or organic acid and or salt of organic or inorganic compound that dissolve in the mixture in the presence of the acid(s).